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Oligosiloles: First Synthesis Based on a Novel Endo-Endo Mode Intramolecular Reductive Cyclization of Diethynylsilanes (SYNTHETIC ORGANIC CHEMISTRY - Synthetic Design)

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derivatives bearing the arylthio group to find that the intermediate iminium ion is trapped by the remaining hydroxy group to afford chiral cyclic imino ethers such as oxazolines.

The reaction described herein may be used as a new chiral pool method from readily accessible chiral oxiranes to chiral amine derivatives with retention of configuration of the chiral carbon [3].

## References

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# Oligosiloles: First Synthesis Based on a Novel *Endo-Endo* Mode Intramolecular Reductive Cyclization of Diethynylsilanes

Kohei Tamao and Shigehiro Yamaguchi

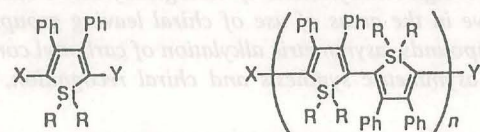
A general and versatile synthesis of 2,5-difunctionalized siloles is developed based on an *endo-endo* mode intramolecular reductive cyclization of diethynylsilanes upon treatment with lithium naphthalenide. With certain functionalized siloles in hand, oligosiloles, from bisiloles to quatersilole, are synthesized by oxidative coupling reaction via higher order cyanocuprates. Structural analysis and electronic properties of the oligosiloles have been investigated by means of X-ray crystallography, NMR studies, and UV-vis spectroscopy.

**Keywords:** 2, 5-Difunctionalized silole/ Intramolecular reductive cyclization/ Oligosiloles/ Oxidative coupling reaction

Silole (silacyclopentadiene) containing  $\pi$ -conjugated polymers have recently been highlighted as a promising candidate for novel  $\pi$ -electronic materials, because of their anticipated properties such as conductivity, thermochromism, and nonlinear optical properties [1]. Polysiloles, silole-2, 5-linked polymers, may be a center of target. Toward the polysilole synthesis, we succeeded in the first general and versatile synthesis of 2,5-difunctionalized siloles via a conceptually new intramolecular reductive cyclization of diethynylsilanes and the first synthesis of oligosiloles as models of the polysiloles by use of functionalized siloles in hand [2].

Bis(phenylethynyl)silane,  $(\text{PhC}\equiv\text{C})_2\text{SiR}_2$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $i\text{-Pr}$ , and  $\text{hexyl}$ ), underwent intramolecular reductive cyclization in an *endo-endo* mode upon treatment with lithium naphthalenide to form 2, 5-dilithiosiloles **1**. This is the first example of intramolecular reductive cyclization of diynes proceeding in an *endo-endo* mode. The compounds **1** were converted into various 2,5-difunctionalized siloles, including 2,5-dibromosilole **2**, 5,5'-Dibromo-2,2'-bisilole **4** and 5,5'''-dibromo-2,2':5',2'':5'',2'''-quatersilole **6**, were prepared by oxidative coupling via higher order cyanocuprate of 2-bromo-5-lithiosilole **3** and 5-bromo-5'-lithio-2,2'-bisilole **5**, respectively. X-ray crystal structures of the bisiloles show highly twisted arrangements between two silole

rings with torsion angle  $62\text{--}63^\circ$ .  $^1\text{H}$  NMR studies on bisiloles show a rapid equilibration between noncoplanar conformers in solution. Despite the noncoplanar arrangement, all of the oligosiloles have unusually long absorption maxima in UV-vis spectra:  $\lambda_{\text{max}}$  (nm) in  $\text{CHCl}_3$ ; bisilole **4**, 416; quatersilole **6**, 443. This remarkable electronic properties may be ascribed to an inherent unique electronic structures of silole ring. The present investigation on oligosiloles as models of polysiloles have enhanced our interests in the still veiled fascinating polysiloles.



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| <b>1</b> ( $\text{X}=\text{Y}=\text{Li}$ )               | <b>4</b> ( $\text{X}=\text{Y}=\text{Br}$ , $n=1$ )               |
| <b>2</b> ( $\text{X}=\text{Y}=\text{Br}$ )               | <b>5</b> ( $\text{X}=\text{Br}$ , $\text{Y}=\text{Li}$ , $n=1$ ) |
| <b>3</b> ( $\text{X}=\text{Br}$ , $\text{Y}=\text{Li}$ ) | <b>6</b> ( $\text{X}=\text{Y}=\text{Br}$ , $n=2$ )               |

## References

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